

# Magnetization Step in Spatially Distorted Heisenberg Kagomé Antiferromagnets

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Motivated by recent experiment for volborthite, a typical spin-1/2 antiferromagnet with kagomé lattice structure, we study magnetization process of classical Heisenberg model on a spatially distorted kagomé lattice using Monte Carlo (MC) method. We find a distortion-induced magnetization step at low temperatures and low magnetic fields. Magnitude of this step is given by  $\Delta m_z = |1 - \alpha|/3\alpha$  at zero temperature, where  $\alpha$  denotes spatial anisotropy in exchange constants. The magnetization step signals a first-order transition at low temperatures, between two phases distinguished by distinct and well developed short-range spin correlations, one characterized by coplanar spin alignment with a  $\sqrt{3} \times \sqrt{3}$  period, and the other by a non-coplanar and partially spin flopped structure. We point out the relevance of our results to the unconventional steps observed in volborthite.

KEYWORDS: volborthite, magnetization step, geometrical frustration, kagomé lattice, Heisenberg model

In antiferromagnets on the kagomé lattice, geometrical frustration effects are believed to suppress the conventional magnetic long-range order and induce large degeneracy of the ground state. It opens a possibility of realizing spin-liquid states, spin analogues of liquids or ices.<sup>1</sup> Volborthite  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  is known as a nearly ideal spin-1/2 kagomé antiferromagnet.<sup>2</sup> Measurements of the magnetization and the specific heat for this compound indicate absence of the conventional magnetic long-range order down to 50 mK.<sup>3,4</sup> Therefore, it is proposed that this material offers an evidence of the quantum spin-liquid state in nature.<sup>4</sup>

Recent studies on volborthite have revealed the existence of unconventional three steps in the magnetization curve.<sup>3</sup> These steps are not anticipated in the magnetization process of isotropic kagomé Heisenberg model in the literature<sup>5,6</sup> and the origin of these steps is not understood. A MC study of the classical Heisenberg model has clarified the existence of the magnetization plateau at one-third of the saturation magnetization ( $m_{\text{sat}}/3$ ) at finite temperatures interpreted as the order by disorder effect.<sup>5</sup> Even for the quantum Heisenberg model ( $S = 1/2$  and 1), exact diagonalization study has shown similar magnetization plateau at zero temperature.<sup>6</sup> However, the magnetization step has not been found at all in the isotropic kagomé Heisenberg model.

In this letter, to shed light on the origin of the unconventional steps observed in volborthite, we calculate the magnetization curve in the antiferromagnetic classical Heisenberg model on the spatially distorted kagomé lattice by using MC method. In our viewpoint, structural distortion, which inevitably exists in volborthite,<sup>4</sup> is a key to explain the magnetization step. This structural distortion induces a spatial anisotropy in exchange interactions. Therefore, as a simple model, we employ an anisotropic ( $J_1$ - $J_2$ ) kagomé Heisenberg model to describe the magnetization process observed in volborthite. We find distortion-induced first-order phase transitions at low temperatures and low magnetic fields. In the vicinity of this first-order phase transition, step-like behaviors

of the magnetization curve are found and spin structure factors change drastically between coplanar and non-coplanar structures. We also determine the  $h$ - $T$  phase diagram for the spatially anisotropic kagomé Heisenberg model.

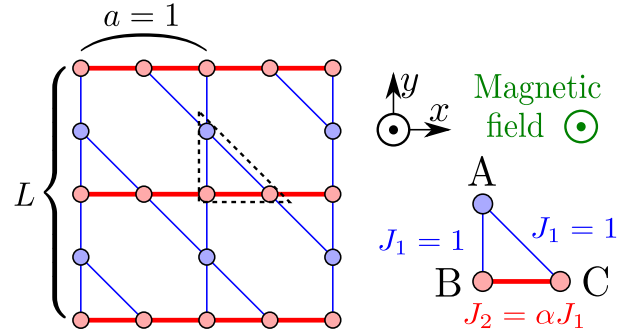


Fig. 1. (Color online) An  $L \times L$  ( $L = 2a$ ) distorted kagomé lattice. Lattice sites labeled by A, B, and C constitute a unit cell (dashed-line triangle). The number of spins is  $N = 3L^2$ . Bonds along two directions have exchange constant  $J_1$  (thin blue lines), while the bond along the third direction has exchange constant  $J_2 = \alpha J_1$  (thick red lines). For volborthite, it is plausible that  $\alpha > 1$ .

Our model Hamiltonian is defined in the form

$$H = J_1 \sum_{\langle i,j \rangle_1} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle i,j \rangle_2} \mathbf{S}_i \cdot \mathbf{S}_j - h \sum_i S_i^z, \quad (1)$$

where  $\mathbf{S}_i$  denotes the Heisenberg classical spin,  $h$  denotes an external magnetic field, and  $\langle i,j \rangle_1$  and  $\langle i,j \rangle_2$  denote nearest-neighbor sites on AB/AC chains and BC chains respectively. In the kagomé lattice, unit cell contains three sites A, B and C, as shown in Fig. 1. The spatial anisotropy induces different antiferromagnetic coupling on each triangle: two  $J_1$  bonds and one  $J_2$  bond. For simplicity, we set  $J_1 = 1$  and  $J_2 = \alpha J_1$ . We simplify the Hamiltonian as

$$H = \sum_{\text{triangles}} \left[ (\mathbf{S}_A \cdot \mathbf{S}_B + \alpha \mathbf{S}_B \cdot \mathbf{S}_C + \mathbf{S}_C \cdot \mathbf{S}_A) \right]$$

$$-\frac{h}{2}(S_A^z + S_B^z + S_C^z)]. \quad (2)$$

The summations are taken over upward and downward triangles. The lattice has no distortion when  $\alpha = 1$ . There are two simple limits for this model. For  $\alpha \rightarrow 0$ , the lattice becomes a decorated square lattice, with additional sites at the midpoints of square lattice edges. In this limit, the ground state is ferrimagnetic. While for  $\alpha \rightarrow \infty$ , the lattice becomes isolated antiferromagnetic chains and free spins, which is equivalent to the one-dimensional lattice. In volborthite, we infer that  $\alpha$  is larger than unity from comparison of bond lengths. The magnitude of the anisotropy is estimated to be less than 20% from theoretical analysis.<sup>7</sup> We consider both kinds of anisotropy, especially  $\alpha = 1.05$  and  $\alpha = 0.95$ , but perform detailed analyses on the  $\alpha = 1.05$  case.

We clarify thermodynamic properties of this model by using MC simulations. The Metropolis algorithm has been employed. We start the simulations from random initial states. Spins are updated in the sequential order on the lattice. We also perform one over-relaxation update per one MC step to accelerate efficient sampling.<sup>8</sup> At every temperature and field,  $5 \times 10^4$  MC steps were taken for equilibration. These are followed by measurements done during more than  $5 \times 10^5$  MC steps. Finally, the results have been averaged over more than 8 independent runs to estimate statistical errors. At low temperatures  $T \leq 0.01$ , we use exchange MC algorithm.<sup>9</sup> Simulations were done for the system size up to  $L = 72$  ( $N = 15552$ ) under the periodic boundary conditions. We set the Boltzmann constant  $k_B = 1$ .

In Fig. 2 (a), we show magnetization  $m_z$  parallel to applied fields at several choices of temperatures as a function of magnetic fields. For both  $\alpha > 1$  and  $\alpha < 1$ , we have observed a magnetization plateau  $m_{\text{sat}}/3$  at low temperatures, which have already been reported by Zhitomirsky for isotropic ( $\alpha = 1$ ) kagomé lattice. Due to the distortion, the magnetization plateau becomes much wider. This tendency is consistent with the results of the exact diagonalization for spin-1/2 distorted kagomé Heisenberg model.<sup>6</sup>

As shown in Fig. 2 (b), we have observed step-like behaviors at low temperatures and low magnetic fields. To see whether these step-like behaviors are the first-order phase transitions in the thermodynamic limit, we calculate the energy distribution  $P(E)$  up to  $L = 72$  ( $N = 15552$ ). If the transition is of the first-order, the energy distribution  $P(E)$  should be bimodal at the transition temperature. As shown in Fig. 2 (c), we find a clear two-peak structure around the transition point. This result shows an evidence for the first-order phase transition at low temperatures. These first-order phase transitions appear only when the lattice has the anisotropies ( $\alpha \neq 1$ ). The transition field increases monotonically with increasing temperatures. The first-order jump becomes reduced with increasing temperatures and vanishes at a finite-temperature critical point as we detail below.

The origin of the first-order phase transitions is well understood by considering zero temperature limit. To an-

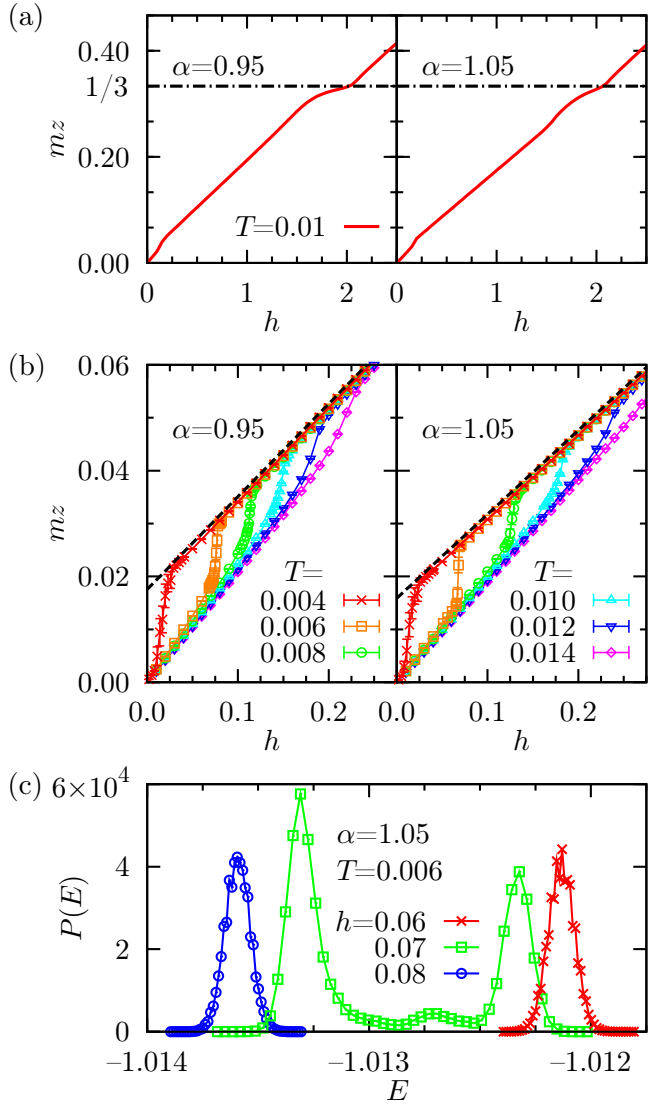


Fig. 2. (Color online) (a) Magnetization curves at  $T = 0.01$  for  $\alpha = 1.05$  and  $\alpha = 0.95$ . The system size is  $L = 36$ . The dashed-dotted line denotes one third of the saturation magnetization. For both anisotropies, magnetization plateaus exist at  $h \simeq 2$ . (b) Magnetization curves at low magnetic fields. Step-like behaviors in the magnetization curve are observed for both  $\alpha = 1.05$  and  $\alpha = 0.95$ . The system size is  $L = 36$ . The step shows first-order transitions below the critical temperature  $T_c \simeq 0.007$ . At  $T > T_c$ , the step vanishes and turns into a crossover. We have observed a magnetization hysteresis for  $T \leq 0.008$ . Statistical errors are smaller than the symbol size at  $T = 0.008$ . Magnetization curves in the decreasing field are shown at  $T \leq 0.006$ . Due to finite size effects, a first-order step at  $T = 0.004$  appears to be rounded. The dashed line denotes the magnetization at  $T = 0$  given by  $m_z = (h + 2|1 - \alpha|)/(6\alpha)$ . See the text for details. (c) Energy distribution  $P(E)$  at several magnetic fields for  $T = 0.006$ . The system size is  $L = 60$ . It shows two-peak structure around the transition point (see the case of  $h = 0.07$ ).

alyze the ground-state properties, we rewrite the Hamiltonian as

$$H = \sum_{\text{triangles}} \left[ \frac{\alpha}{2} \left( \mathbf{S}_{\Delta} - \frac{h}{2\alpha} \mathbf{e}_z \right)^2 + \frac{1-\alpha}{2\alpha} h S_A^z + \text{const.} \right], \quad (3)$$

where  $\mathbf{S}_{\Delta} = \mathbf{S}_A/\alpha + \mathbf{S}_B + \mathbf{S}_C$ . For  $h = 0$ , the energy is minimized with  $\mathbf{S}_{\Delta} = 0$ . The ground state,

which satisfies the constraint  $\mathbf{S}_\Delta = 0$ , has an infinite degeneracy and the magnetization is zero. While for  $0 < h < \min(2, 4\alpha - 2)$ , the energy is minimized with  $\mathbf{S}_\Delta = (h/2\alpha)\mathbf{e}_z$ ,  $S_A^z = -\text{sign}(1 - \alpha)$ , and hence  $S_B^z = S_C^z = [h + 2\text{sign}(1 - \alpha)]/(4\alpha)$ . Therefore, at zero temperature, we obtain the magnetization as

$$m_z = \frac{S_A^z + S_B^z + S_C^z}{3} = \frac{h + 2|1 - \alpha|}{6\alpha}. \quad (4)$$

Equation (4) indicates that the magnetization jumps by infinitesimal magnetic field at  $T = 0$ . Although thermal fluctuations reduce the magnitude of this jump and shift the transition point to higher fields, this first-order phase transition still survives at sufficiently low temperatures as we have already shown by MC calculations.

From the above analyses, it turns out that the origin of the first-order phase transition is the switching of the ground state by a level crossing. When the spatial anisotropy exists, macroscopic degeneracy of the kagomé antiferromagnet is partially lifted by the infinitesimal magnetic field, i.e., under the magnetic fields, the ordered vector becomes  $\mathbf{q} = (0, q_y)$ , where the range of  $q_y$  is given by  $-\pi \leq q_y \leq \pi$ .

To identify the nature of the first-order transition, we calculate at  $T > 0$  the spin structure factors defined as

$$S^{xy}(\mathbf{q}) = \frac{1}{N^2} \sum_{l,i,j} \langle \mathbf{S}_l^x \cdot \mathbf{S}_{l+j}^x + \mathbf{S}_l^y \cdot \mathbf{S}_{l+j}^y \rangle e^{i\mathbf{q} \cdot (\mathbf{R}_l - \mathbf{R}_j)}, \quad (5)$$

where the index  $l$  denotes the positions of the three sites on the unit cell, and  $i, j$ , and  $\mathbf{R}_{i,j}$  denote the coordinate of the  $(i, j)$ -th unit cell on the triangular Bravais lattice. We use the dimensionless units in which the lattice period (length of the square in Fig. 1) is taken unity and hence the interspin distance equals  $1/2$ . The first Brillouin zone is a square bounded by  $-\pi \leq q_x, q_y \leq \pi$ .

As shown in Fig. 3, the structure factors  $S^{xy}(\mathbf{q})$  drastically change when we cross the first-order transition point. At lower fields [ $h = 0.1$ ,  $T = 0.01$ , see Fig. 3 (b)],  $S^{xy}(\mathbf{q})$  has broad peaks at  $\mathbf{q} = (\pm 2\pi/3, \mp 2\pi/3)$ , which corresponds to  $\sqrt{3} \times \sqrt{3}$  pattern with the  $120^\circ$  structure in real space. At higher fields [ $h = 0.2$ ,  $T = 0.01$ , see Fig. 3 (c)], the structure factor has sharp peaks at  $\mathbf{q} = (0, \pm\pi)$ , signaling the real space pattern shown in the lower panel of Fig. 3 (c). In the magnetic structures in Fig. 3 (c), spins on A sites align parallel to the magnetic field indicating a partial spin flip under magnetic fields. Along a BC chain, the  $xy$  components of spins on the B sites are all parallel each other and are antiparallel to all the spins on the C sites. Along an AB chain, the spins on the B sites align alternatingly. Although the ground states are degenerate among any ordered vector  $\mathbf{q} = (0, q_y)$ , thermal fluctuations appear to favor the  $\mathbf{q} = (0, \pm\pi)$  configuration via the order by disorder effect.<sup>10,11</sup>

We obtain phase boundaries for  $\alpha = 1.05$  at lower temperatures and lower fields  $h < 2$ . From the location of the steps, we determine the first-order transition line. Because this first-order transition does not involve any explicit symmetry breaking, its nature is essentially the same as that of gas-liquid type. Thus, the

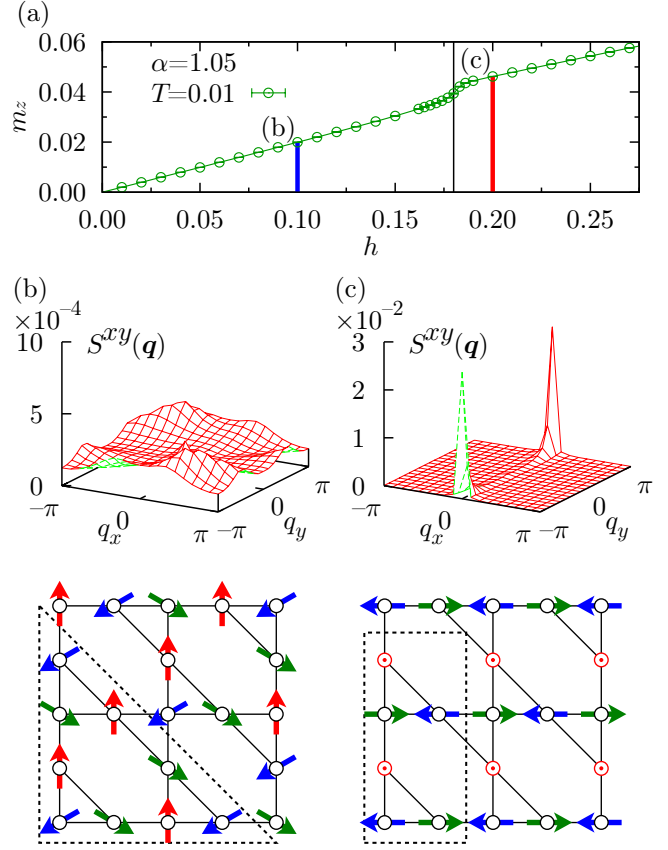


Fig. 3. (Color online) (a) Magnetization curve around the first-order transition at  $T = 0.01$ . (b) and (c) Spin structure factors for  $\alpha = 1.05$ ,  $L = 36$  (upper panel) and corresponding schematic spin configurations in real space (lower panel) around the first-order transition. In (b),  $h$  is lower than the transition field  $h_c \simeq 0.16$  ( $h = 0.1$ ,  $T = 0.01$ ), where the structure factor shows a  $\sqrt{3} \times \sqrt{3}$  pattern. In (c),  $h$  is higher than  $h_c$  ( $h = 0.2$ ,  $T = 0.01$ ), where the structure factor shows a  $\mathbf{q} = (0, \pm\pi)$  pattern. In spin structure factors, we illustrate the region  $-\pi \leq q_x \leq \pi$  and  $-\pi \leq q_y \leq \pi$  in the momentum space. In schematic spin configurations illustrated in the lower panels of (b) and (c), the unit cells of each pattern are shown in dotted-line.

first-order phase transition line terminates at the critical point and a crossover line exists beyond the critical point. This crossover line is characterized by the peak of the specific heat and the susceptibility. The universality class of the critical point of the gas-liquid transition belongs to that of two-dimensional Ising model.<sup>12</sup> Therefore, along the crossover line, the susceptibility  $\chi$  has the singularity  $\chi_{\text{peak}} \propto |T - T_c|^{-\gamma}$  or  $|h - h_c|^{-\gamma}$ , where  $\gamma = 7/4$  near the critical point.<sup>12</sup> By using this relation, we roughly estimate location of the critical point as  $(h_c, T_c) = [0.11(1), 0.007(1)]$ .

Although continuous symmetry breaking is prohibited in two dimensions at  $T \neq 0$ , a quasi-long-range order may occur for the case of the XY anisotropy.<sup>13</sup> Because the effective symmetry of the Heisenberg model becomes XY type under the magnetic fields, the quasi-long-range order, i.e., Berezinsky-Kosterlitz-Thouless (BKT) transition may occur,<sup>14-17</sup> although at  $T = 0$  the system becomes effectively disconnected BC chains. In order to examine the possibility of the quasi-long-range order, we have calculated the spin correlation function and esti-

mated the correlation lengths below the crossover line. We find that the spin correlations along the AB and BC chains decay exponentially for system size  $L \geq 48$  even at the lowest accessible temperature. Therefore, we conclude that no BKT phase exists under magnetic fields.

We now examine the relevance of our results to the unconventional steps observed in volborthite. In our model, we find one distortion-induced magnetization step. This first-order transition is similar to the step-like behaviors in volborthite, though three steps are observed in the experiment. To identify the relationship between the experiment and the result of our model, we estimate the upper bound of the magnetization step. Since the distortion is 20% at most, we obtain  $\Delta m_z = (\alpha - 1)/(3\alpha) < 1/18$  at  $T = 0$  from eq. (4). At  $T \neq 0$ , the jump occurs between two nonzero  $m_z$ 's at  $h \neq 0$  and as a first look, it would not specify the magnetization at the step. Nevertheless the jump size  $\Delta m_z$  is less than the jump at  $T = 0$  and  $m_z$  after the jump with increasing field  $h$  is at most twice of  $\Delta m_z$  at  $T = 0$ . By considering the magnitude of the three steps  $m_{\text{sat}}/3$ ,  $m_{\text{sat}}/6$ , and  $m_{\text{sat}}/45$  in the experiment, if we assign our jump to one of the experimental jumps, it is likely that the  $m_{\text{sat}}/45$  step corresponds to the present distortion-induced step. The sudden change in the spin structure factors from  $\mathbf{q} = (\pm 2\pi/3, \mp 2\pi/3)$  to  $\mathbf{q} = (0, \pm\pi)$  structures at the first-order transition may be detected in neutron scattering and nuclear magnetic resonance experiments.

In the experiment,  $m_z$  at the step does not sensitively depend on  $T$ , while our results imply that it should decrease to  $m_z = 0$  when  $T \rightarrow 0$ . This discrepancy may be due to quantum effects under which  $\mathbf{q} = (\pm 2\pi/3, \mp 2\pi/3)$  structure may be stabilized even at  $h \neq 0$  and  $T = 0$ . It is intriguing to identify the critical point for volborthite and see whether the first-order transition survives under quantum fluctuations.

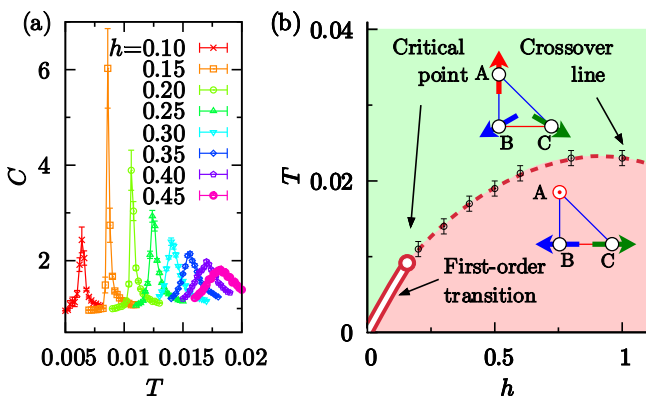


Fig. 4. (Color online) (a) Temperature dependence of specific heat at several magnetic fields which are labeled from  $h = 0.10$  to 0.45 starting from the left ( $\alpha = 1.05$ ,  $L = 60$ ). (b) Phase diagram of distorted kagomé lattice ( $\alpha = 1.05$ ). The first-order phase transition line terminates at the critical point (open circle). Dashed line represents a crossover line, which is characterized by the peak of the specific heat.

In summary, by using the MC method, we have clarified thermodynamic properties of the classical Heisenberg antiferromagnets on a distorted kagomé lattice under magnetic fields. The distortion-induced magnetization step appears at low temperatures and low magnetic fields. Estimating the upper bound of the step size, we conclude that this is the first-order transition induced by the spatial anisotropy and corresponds to the step at the lowest field observed for volborthite. The spin structure factor shows a sharp change at the transition which may be detected experimentally.

Clarifying the origins of two other steps in the experiment remains for future studies. Other interactions in volborthite such as next-nearest neighbor interactions and Dzyaloshinsky-Moriya interactions may give rise to additional unconventional phase transitions. Besides, our results are obtained for the classical model while volborthite consists of quantum spin-1/2 spins. It is an interesting future issue whether the quantum fluctuations suppress the first-order transition observed in the classical system, leading to a crossover with a similarity to the experiment where temperature dependence of the transition field is weak.

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